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Shift of phonon anomaly with T_c observed in (Y,Er)$Ba_2Cu_3O_{7-\delta}$ by ion channeling

R. P. Sharma, L. E. Rehn, P. M. Baldo, and J. Z. Liu
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439
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Ion channeling and Rutherford backscattering (RBS) in small, high-quality single crystals of (Y,Er)$Ba_2Cu_3O_{7-\delta}$ has previously shown an abrupt anomaly at T_c in displacements perpendicular to the c axis of atoms in the [001] Cu-O rows. Here we report additional RBS-channeling results, and new characteristic x-ray measurements that permit more direct identification of the displacements of the individual atomic species in both materials. It is demonstrated that the observed phonon anomaly shifts directly with stoichiometry-induced changes in T_c.

Although considerable interest exists in determining the degree to which phonons contribute to the superconducting-pairing mechanism in the class of high-T_c compounds denoted by $RBa_2Cu_3O_{7-\delta}$, (where R denotes rare earth), experimental determinations of phonon properties in these materials are difficult because only relatively small ($1\times2\times0.05$ mm^3) high-quality single crystals are available. Evidence suggesting phonon changes at T_c in these compounds has been obtained from x-ray[1] and neutron diffraction,[2,3] elastic constant measurements,[4,5] and Raman[6-8] studies. However, the observed effects are typically small, and their interpretation remains controversial.

We have previously reported ion channeling and Rutherford backscattering (RBS) studies in high-quality single crystals of $YBa_2Cu_3O_{7-\delta}$ showing a clear, abrupt anomaly at T_c in atomic displacements perpendicular to the c axis.[9] Replacing Y by Er (higher atomic number and mass) made it possible to isolate the channeling effect of the [001] Er-Ba rows in the RBS channeling results, but not that of the Cu-O rows.[10] A simple analysis yielded normal, Debye-type behavior for the Er and Ba atoms, demonstrating that the phonon anomaly was due solely to displacements of atoms in the Cu-O rows.

In this Rapid Communication, we report ion channeling combined with RBS and characteristic x-ray measurements in both $YBa_2Cu_3O_{7-\delta}$ and $ErBa_2Cu_3O_{7-\delta}$ single crystals. The new results permit more direct identification of the contributions from individual atomic species to the observed phenomena. In particular, the x-ray measurements allow the contribution from the [001] Cu-O rows to be isolated. These results confirm that small displacements of Cu and O atoms perpendicular to the [001] direction are responsible for the phonon anomaly at T_c.[10] In addition, we demonstrate that the observed anomalous behavior shifts directly with stoichiometry induced changes in T_c, suggesting a causal link between the phonon anomaly and the superconducting transition.

Ion channeling results from a correlated sequence of small-angle collisions produced when an energetic ion beam is closely ($\leq 1°$) aligned with a major crystallographic direction. This steering, or channeling effect, causes a large reduction in small-impact parameter events such as Rutherford backscattering (RBS) and innershell, characteristic x-ray production. The critical angle[11] of incidence for channeling is determined by the ion energy, the atomic numbers of the projectile and target, the interatomic spacings, and any displacements (static or thermal) of the atoms from their perfect lattice sites. Measurements of characteristic x-ray production permit the displacements of the individual atomic species to be extracted more accurately than can be done using RBS. Ion channeling is quite sensitive to changes in phonon properties since it provides a direct, real-space probe capable of measuring very small (≤ 0.001 nm) atomic displacements. In addition, the channeling technique is fully compatible with the existing small but high-quality single crystals.

Mirrorlike single crystals of $YBa_2Cu_3O_{7-\delta}$ and $ErBa_2Cu_3O_{7-\delta}$ in the form of thin (≤ 100 μm) flakes approximately 1–2 mm^2 in area were grown by a nonstoichiometric melting method, then annealed in flowing oxygen for 72 h at 500 °C. Magnetic shielding measurements showed a sharp (~ 1 K in width) superconducting transition at $T_c > 92$ K. A few of both the Y and Er crystals were annealed a second time for 66 h at 520 °C in a nitrogen atmosphere containing 1.6% oxygen, to produce an oxygen stoichiometry of $O_{6.6}$. Subsequent magnetic shielding measurements showed that the superconducting transition remained sharp, but as expected, T_c had shifted to 54 K in both materials. Additional specimens were annealed in a similar manner in nitrogen containing 75-ppm oxygen to produce nonsuperconducting crystals with an oxygen stoichiometry of O_6.

The crystals were mounted using a metal-containing epoxy on a precision double-axis goniometer (angular resolution 0.01°); the 0.5-mm-diameter analysis beam (either 1.5- or 6.0-MeV ^{4}He) was collimated to a divergence $\leq 0.05°$. A solid-state RBS detector (FWHM = 16 keV; 30 mm^2 area) was placed approximately 4 cm from the specimen at a scattering angle of 165°. A windowless, liquid-nitrogen cooled Si(Li) x-ray detector, 30 mm^2 in area, with an energy resolution of < 200 eV at 8 keV, was mounted ~ 5 cm from the specimen at a scattering angle of 142°. This distance could be varied using a special attachment provided in the cryostat. Aluminum foil, approximately 25 μm thick, was used to protect the x-ray detector from the backscattered alpha particles. The vacuum in the chamber was maintained at $(3\text{–}4)\times10^{-9}$ torr during analysis. Cooling was accomplished via a closedcycle He-refrigeration unit capable of stabilizing the specimen temperature to within ±3° between 30 and 300 K. The total dose in any one analyzed area was kept below 400 nC because of the sensitivity of these materials to irradiation damage.[12]

A beam of 6.0-MeV He ions was used for the x-ray measurements. The higher energy is advantageous, because the cross section[13] for generating 8.047-keV Cu $K\alpha$ x rays increases by almost 2 orders of magnitude in going from 1.5 to 6.0 MeV. Although the cross section for L-shell x-ray production is even greater, the approximately ten times larger L-shell electron orbital radii[14] (~0.01 nm) in Cu, make L-shell measurements considerably less sensitive than K-shell data to small atomic displacements.

[001] axial scans of an $YBa_2Cu_3O_{6.6}$ (T_c = 54 K) crystal taken with 1.5-MeV He at temperatures of 42, 63, 80, and 100 K are shown in Fig. 1. The RBS energy acceptance gate was the same as used previously,[9] that is from just below the Cu leading edge to just above that of O. The RBS yield in Fig. 1 therefore contains combined information from Y, Ba, and Cu displacements, to a depth of ~700 nm below the surface. The minimum yield (4–5)% of random, is higher than the (1–2)% observed

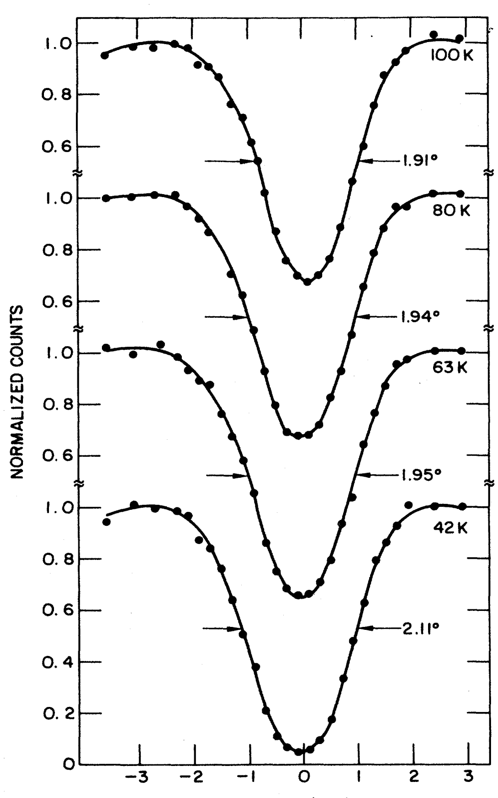

FIG. 1. [001] axial channeling RBS scans measured at temperatures of 100, 80, 63, and 42 K with 1.5-MeV ^{4}He incident on an $YBa_2Cu_3O_{7-\delta}$ single crystal with a T_c of 54 K. The RBS gate was set to accept accounts from just below the Cu leading edge to just above that of O. The yield therefore contains combined information on Y, Ba, and Cu displacements from a depth of ~700 nm.

previously in specimens with a T_c of 92 K. This suggests some deterioration in the crystal quality following the second anneal, but still indicates a reasonably good crystal.[15] Previously, an abrupt increase of (7–8)% in the full width at half maximum (FWHM) of the [001] axial RBS scan was measured between 100 and 80 K in specimens with a T_c of 92–93 K.[9,10] The FWHM of the axial scans in Fig. 1 show only a small increase between 100 and 63 K, consistent with the small decrease in thermal vibration amplitude expected at these low temperatures. However, the abrupt increase in the FWHM of ~8% does occur when the measurement temperature is lowered further, through T_c at 54 K. Additional scans taken alternatively above and below 54 K confirmed that the observed anomalous increase between 63 and 42 K was not due to any beam-induced damage. In one of the specimens that had a stoichiometry of O_6, magnetic shielding showed no evidence for a superconducting transition down to 4.2 K, and no anomalous increase in the FWHM of channeling scans was seen down to the lowest measurement temperature of 30 K. The shift of the anomalous increase with T_c demonstrates a fundamental link between the phonon anomaly and the superconducting transition.

Similar [001] axial scans taken at the same four temperatures using Cu $K\alpha$ x rays produced by 6-MeV ^{4}He incident on an $ErBa_2Cu_3O_{6.6}$ (T_c = 54 K) crystal are shown in Fig. 2. The cross section[13] for Cu $K\alpha$ production decreases by about 90% in going from 6 to 2.5 MeV, which corresponds to a depth about 10 μm below the surface. Also, the 8-keV x rays are attenuated[16] by 90% over approximately the same depth interval. Hence the yield in Fig. 2 contains information on Cu atom displacements averaged over a depth of many microns. This large depth explains the increase in minimum yield from (4–5)% to ~7% between Figs. 1 and 2. The narrower width of the axial scans in Fig. 2 compared to Fig. 1 is due primarily to the inverse square-root dependence of the FWHM on the incident-ion energy.[11] Again, only a slight change in the FWHM of the axial scans in Fig. 2 is seen between temperatures of 100 and 63 K, but an abrupt increase (~10%) is seen as the measurement temperature is lowered through the superconducting transition at 54 K. Remember that the data in Fig. 1 contain combined information on the Y, Ba, and Cu displacements, while that in Fig. 2 isolates the contribution from only the Cu displacements. The fact that the relative jump in the FWHM at T_c is greater in Fig. 2 than in Fig. 1 therefore supports our previous interpretation[9] that the change is due solely to vibrations of Cu and O atoms. In this regard, no significant change was observed in scans above and below T_c with either the Y, Ba, or Er L-shell x rays. Since the L-shell radii for these high-Z materials are relatively small (~0.003 nm), the L x-ray results also support the earlier interpretation.

Quantitative analysis of channeling data in polyatomic crystals containing different elements and/or different interatomic spacings is complex.[17] In the $RBa_2Cu_3O_{7-\delta}$ structure, four different atomic rows are found parallel to the [001] axis: one is an alternating sequence of one R and two Ba atoms; a second consists of one Cu atom and a Cu atom pair, separated by single O atoms; two additional

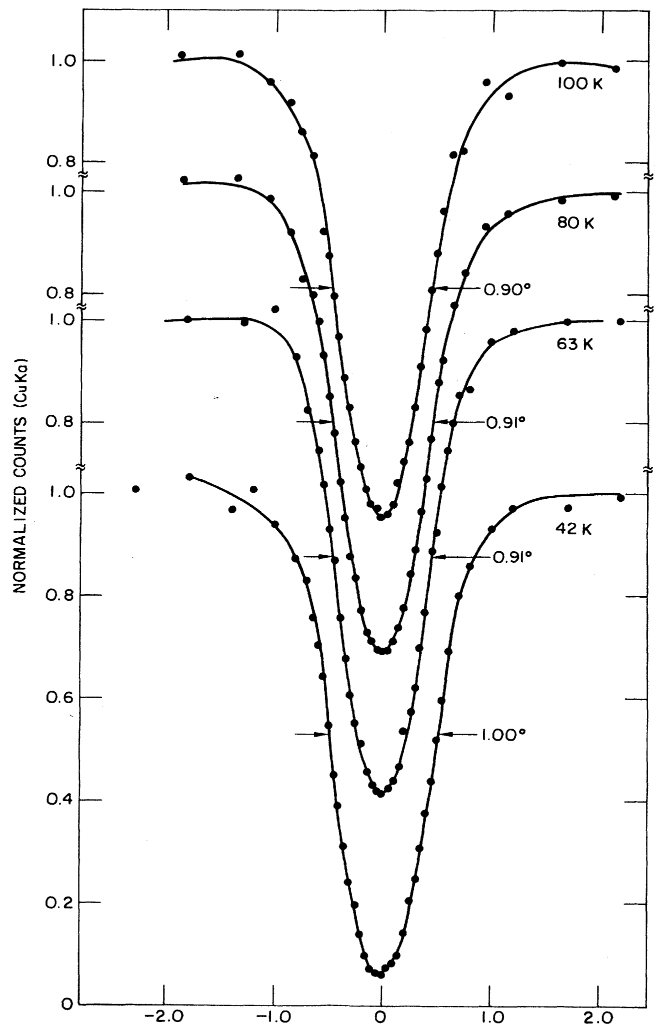

FIG. 2. As in Fig. 1, only now the yield is Cu $K\alpha$ x-ray production by 6-MeV ^{4}He incident on an $ErBa_2Cu_3O_{6.6}$ single crystal with a T_c of 54 K. Information on the atomic displacements in the Cu-O rows is isolated in these measurements.

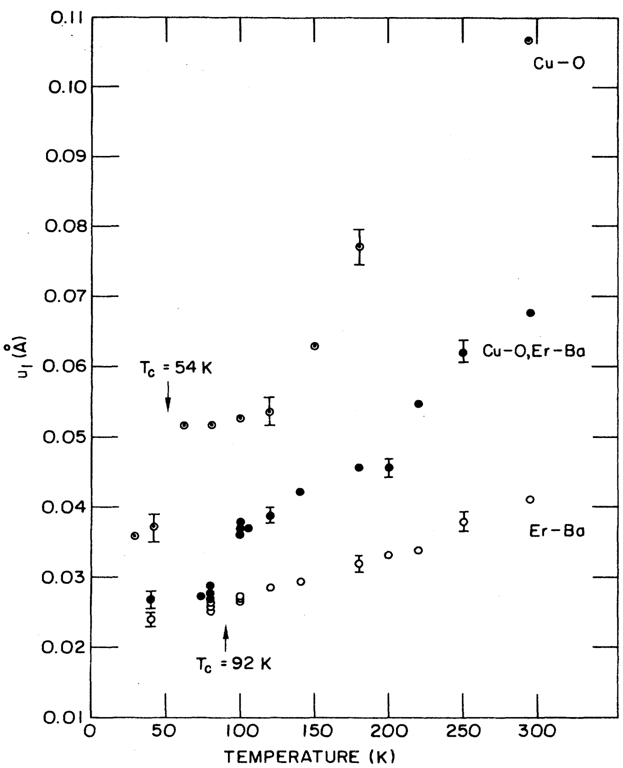

FIG. 3. Average vibrational amplitude, u_1, extracted from (upper curve, dotted circles) x-ray scans such as shown in Fig. 2, and (middle curve, solid circles; lower curve, open circles) from 1.5-MeV ^{4}He RBS scans on an $ErBa_2Cu_3O_{7-\delta}$ crystal with T_c =92 K.

rows contain only O atoms, each with different interatomic spacings. We can neglect any contribution from the two [001] O rows because of their weak channeling effect (low atomic number and large interatomic distances). If we further assume that the changes in the FWHM in Fig. 2 are due entirely to changes in the vibrations of atoms on the Cu-O rows, the average vibration amplitude, u_1, perpendicular to the [001] axis can be extracted using the continuum model[18] (with corrections based upon the Monte Carlo computer simulations of Barrett[19]) and the averaging procedure described previously.[9] The u_1 values extracted in this manner from the [001] Cu $K\alpha$ x-ray scans are indicated as a function of temperature by the dotted circles in Fig. 3. For comparison, previous results from a similar analysis of 1.5-MeV He RBS scans for the Cu-O and Er-Ba rows combined (solid circles) and for the isolated Er-Ba row (open circles) are also shown.

As anticipated, the largest changes in amplitude are seen to occur for atoms in the Cu-O rows. Previously, by subtracting point by point the normalized Er-Ba RBS axial scans from twice the combined Er-Ba-Cu RBS data, we estimated[9] the change across T_c in u_1 for Cu to be from 0.0043 to 0.0055 nm. The actual values obtained by using the Cu $K\alpha$ signal to isolate the Cu-O amplitude is seen from Fig. 3 to be 0.0037 to 0.0052 nm. The agreement is very good, especially considering that a small increase in vibration amplitude is expected between 54 and 92 K.

Although the channeling evidence for an anomaly in the displacements of the Cu and O atoms at T_c is overwhelming, the implication of a large change in Debye properties at the superconducting transition clearly conflicts with other reported changes[1,4,5,20,21] that are much smaller, only one part in 10^3 or less. As pointed out earlier,[9,10] a more realistic interpretation of the anomalous jump in the FWHM across T_c would include introducing correlations between the displacements of the Cu and O atoms in the superconducting state. That is, the *relative* displacements of the atoms in the [001] Cu-O rows become less, producing a smoother string of atoms below T_c. A smoother atomic row will increase the FWHM due to more effective shadowing of underlying neighboring atoms on the row. Oen[22] has reported that scattering from a second nearest neighbor can increase the FWHM by about 10%, which is the magnitude of change that is observed. He further comments that the effect of correlated displacements will be largest near the bottom of the axial scan, which also has been reported.[23] For these reasons, we believe that the abrupt increase in the FWHM of the axial scans at T_c indicates that the displacements perpendicular to the c axis of the atoms in the Cu-O rows become strongly correlated in the superconducting state.

There remains the possibility that static atom displacements (fictive phonons), rather than dynamic thermal displacements, are responsible for the change observed at T_c.[23] Because the velocity of MeV He ions (10^9 cm/s) is much greater than that of thermal vibrations (10^5 cm/s), such channeling cannot distinguish between static and thermal displacements. Egami and co-workers[24] have proposed that microdomains of small static displacements contribute to the high transition temperature (105 K) of $Tl_2Ba_2CaCu_2O_8$, and more recently have suggested[25] that similar static displacements may occur in $YBa_2Cu_3O_{7-\delta}$. Whether the displacements are static or dynamic our results, which clearly reveal wider axial scans below T_c, imply more strongly correlated atomic displacements along the [001] Cu-O rows in the superconducting state.

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